# Improving Sustainability and Rubber Security with New Eggshell/Silica Filled Guayule Natural Rubber Composites

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## INTRODUCTION

- Natural rubber (NR) is irreplaceable in current human society, and the U.S. NR supply is all imported;
- Guayule natural rubber (GNR) is an allergy-free [1], sustainable alternative NR, which can be farmed domestically;
- Reinforcing fillers are necessary for rubber composites, but most commercial fillers, like precipitated silica (PS), are synthetic and not renewable;
- As an abundant waste byproduct from the food industry, low cost eggshell (ES) derived filler has the potential to replace unrenewable fillers [2].

## HYPOTHESIS

- ES can reduce the cost of rubber composites by replacing high cost PS in GNR products, and by reducing power consumption;
- Mechanical and dynamic mechanical properties can be enhanced by stronger ES-filler interaction with GNR and more uniform filler dispersion, than achievable in PS-GNR composites.

## METHODS - MATERIAL PREPARATION

- GNR was used as the rubber matrix;
- Three filler loadings were 50, 60 and 70 parts per hundred rubber (phr);
- At each filler loading level, PS (Hi-Sil 190G, PPG Industries Inc) was gradually replaced by ES (Michael Foods) until no PS remained (0 ES to 100% ES) (Fig. 1).

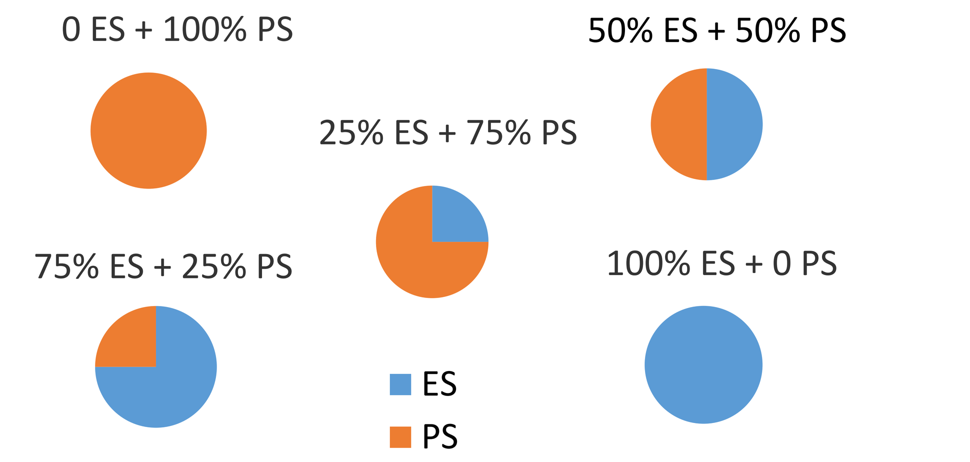


*Fig. 1: Filler composition for each filler loading level (50, 60 and 70 phr)*

## METHODS - CHARACTERIZATION

- Tensile properties were measured according to ASTM D 412;
- Hardness number (Shore A) was measured according to ASTM D 2240;
- Energy consumption for rubber compounding was measured;
- Crosslink density and gel fraction were measured by toluene-swelling test;
- Tan δ (loss modulus over storage modulus) was measured from -90°C to +90 °C. The strain amplitude was 0.1% and frequency was 10 Hz;
- GNR-filler interaction and filler dispersion were characterized by scanning electron microscopy (SEM) of both tensile fracture and cryogenically fractured surfaces;
- Results were analyzed using ANOVA (analysis of variance) and significant differences were claimed at $P \leq 0.05$.

## RESULTS AND DISCUSSION

- Less power was consumed as PS was replaced by ES but more power was required as total loading increased (Fig. 2 a);
- Tensile strength increased with increased ES fraction and was maximal at 60 phr total loading (Fig. 2 b).

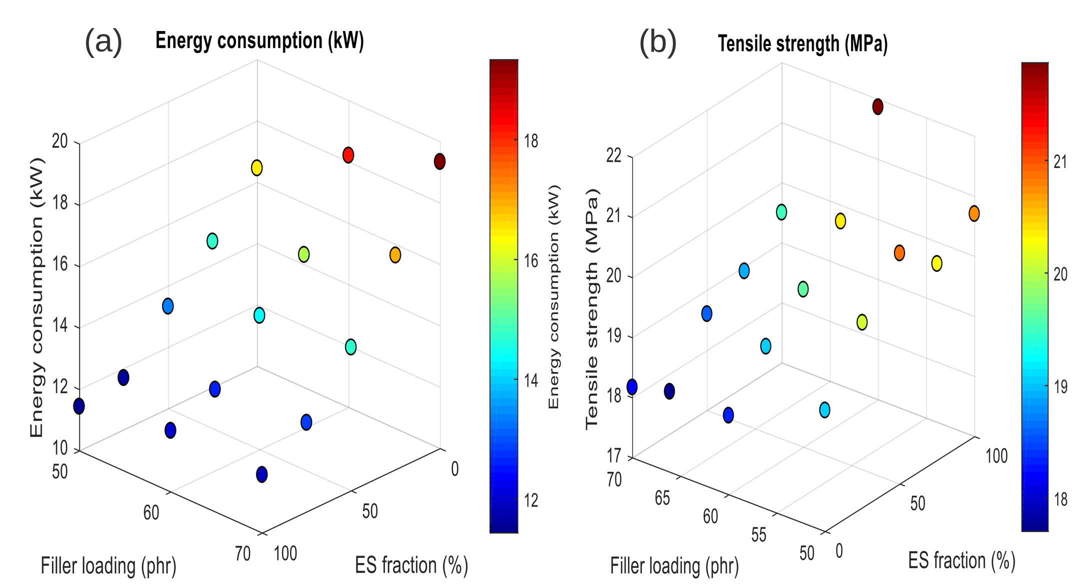


*Fig. 2: (a) Energy consumption during compounding; (b) Tensile strength of ES/PS filled GNR composites*

- Elongation at break increased with increasing ES fraction and with lower filler loadings (Fig. 3 a);
- Increasing ES fraction raised the gel fraction of GNR composites (Fig. 3 b);
- The ES had a strong interaction with GNR as shown by the high gel fraction (Fig. 3 b) and bridge structures (Fig. 4 b, c).

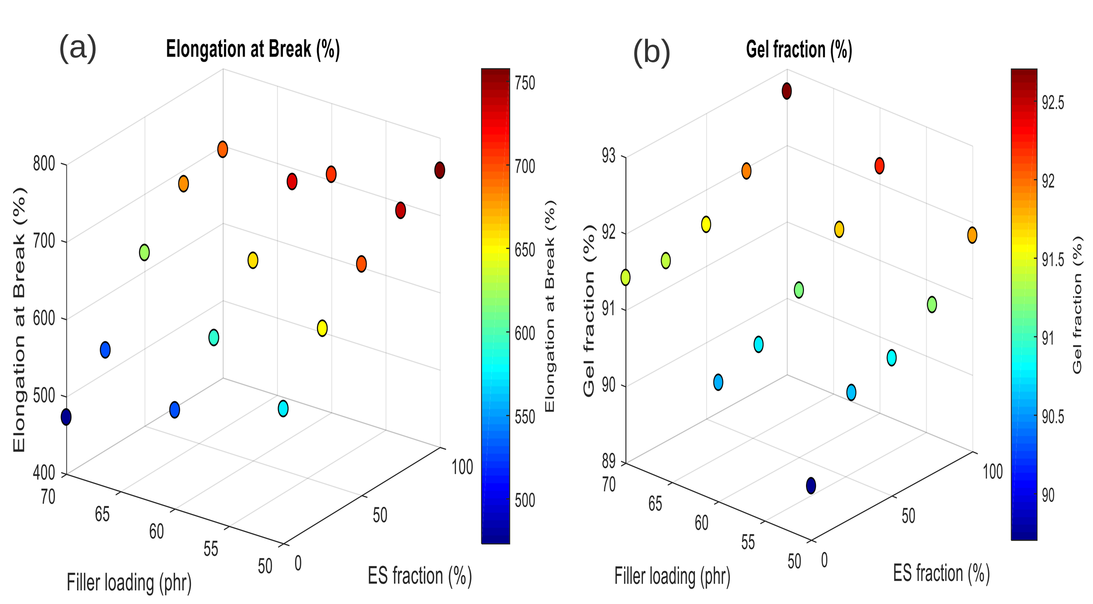


*Fig. 3: (a) Elongation at break; (b) Gel fraction of ES/PS filled GNR composites*

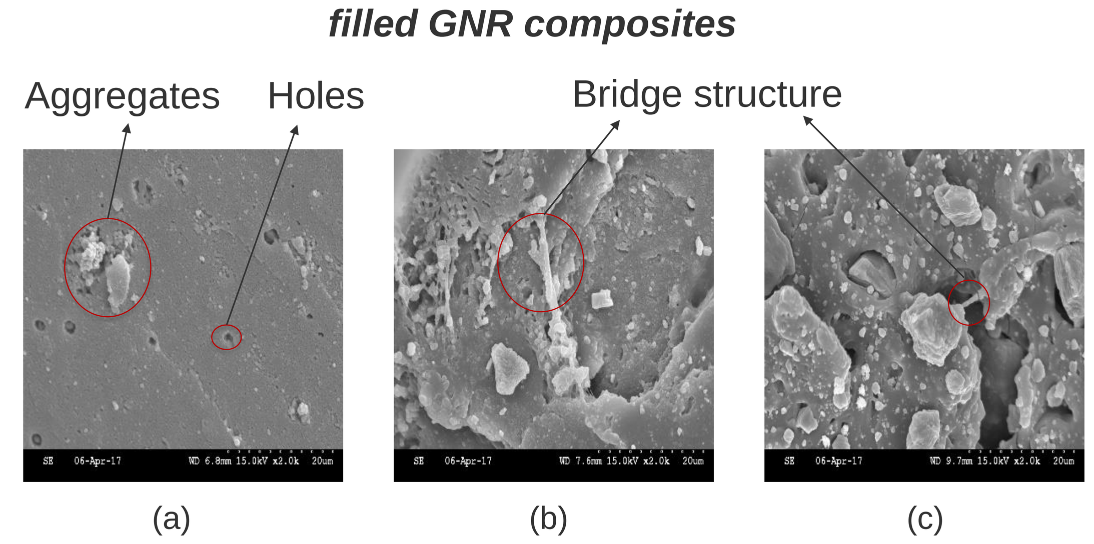


*Fig. 4:Tensile fracture surfaces for 50 phr ES and PS filled GNR: (a) GNR with 0% ES fraction; (b) GNR with 50% ES fraction; (c) GNR with 100% ES fraction*

- PS formed aggregates which weakened the GNR composites (Fig. 4 a and Fig. 5 a);
- The ES was less aggregated in the GNR composites and the more uniform filler dispersion (Fig. 5 b, c) resulted in the higher tensile strength observed (Fig. 2 b).

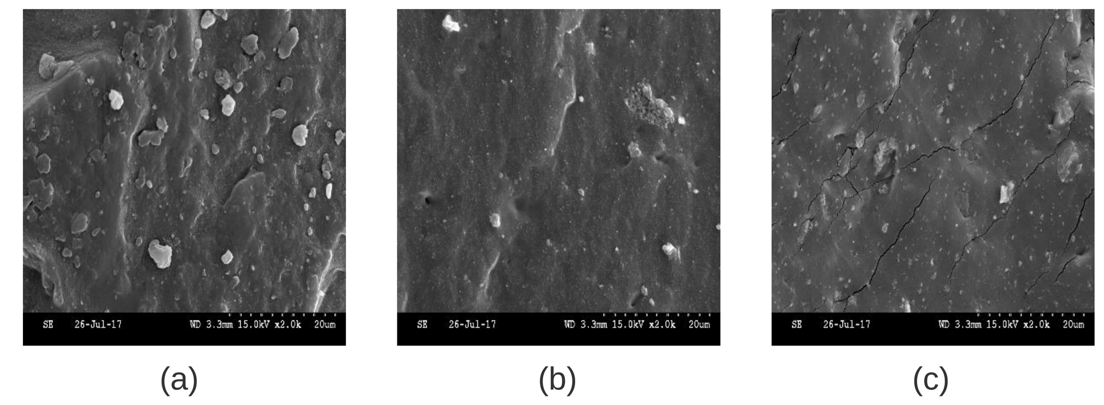


*Fig. 5: Cryogenically fractured surfaces for 50 phr ES and PS filled GNR: (a) GNR with 0% ES fraction; (b) GNR with 50% ES fraction; (c) GNR with 100% ES fraction*

- Modulus at 300% and hardness decreased with increasing ES fraction (Fig. 6 a, b);
- Higher filler loadings increased modulus at 300% strain and caused greater hardness (Fig. 6 a, b).

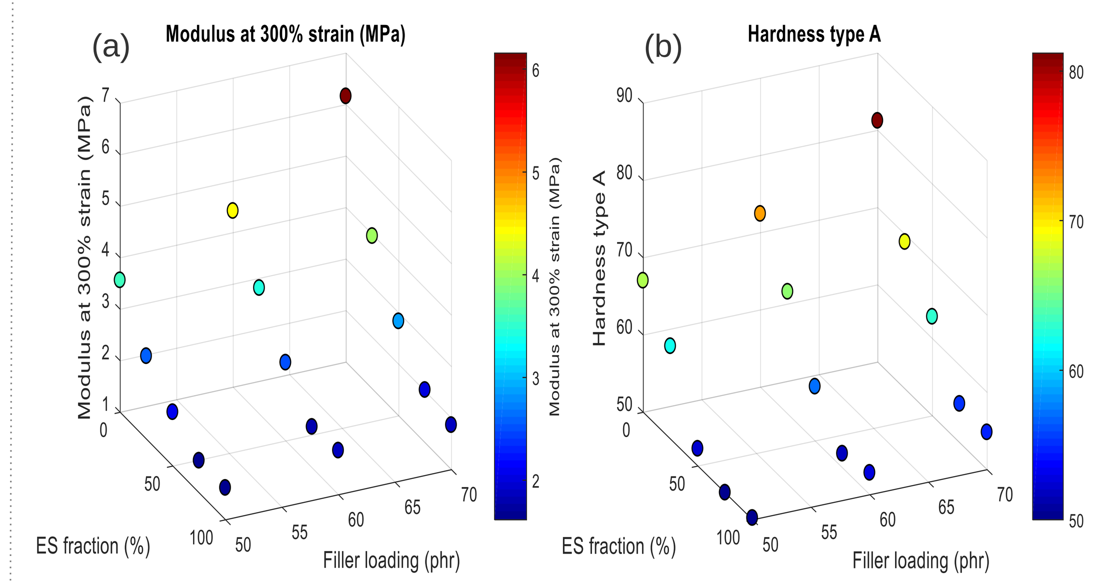


*Fig. 6: (a) Modulus at 300% strain; (b) Hardness type A of ES/PS filled GNR*

- At temperatures below 0°C, tan δ peak values increased with increasing ES fraction, indicating higher rubber chain mobility (Fig. 7 a);
- Above 50°C, tan δ reduced with increasing ES fraction, indicating that ES formed a weaker filler network than PS and had lower energy loss during deformation (Fig. 7 b).

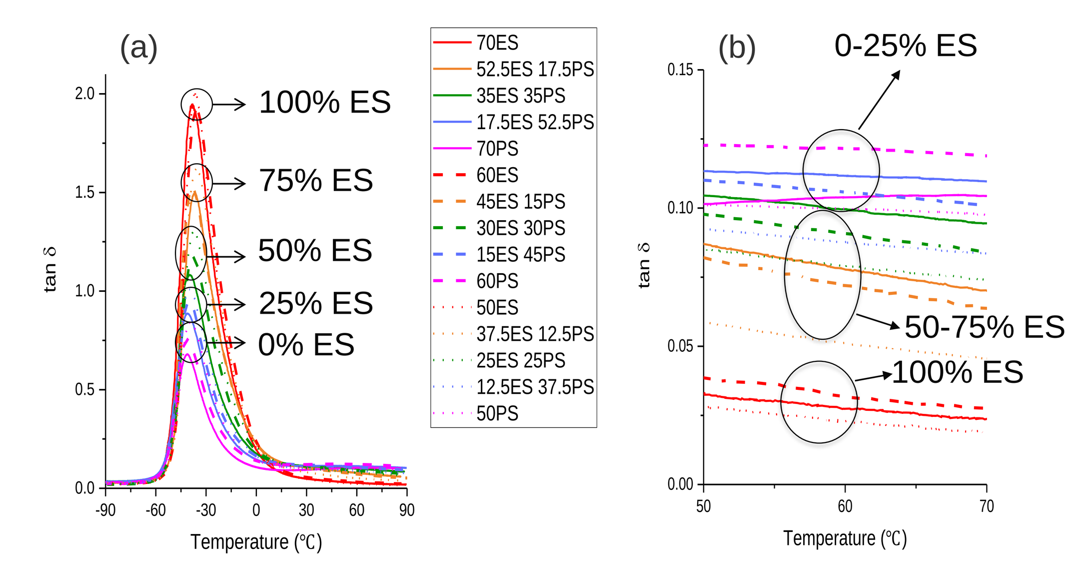


*Fig. 7: Tan δ of ES/PS filled GNR at various temperature (a) -90°C to 90°C; (b) 50°C to 70°C*

- Crosslink density decreased as ES fraction increased and with increasing filler loading (Fig. 8).

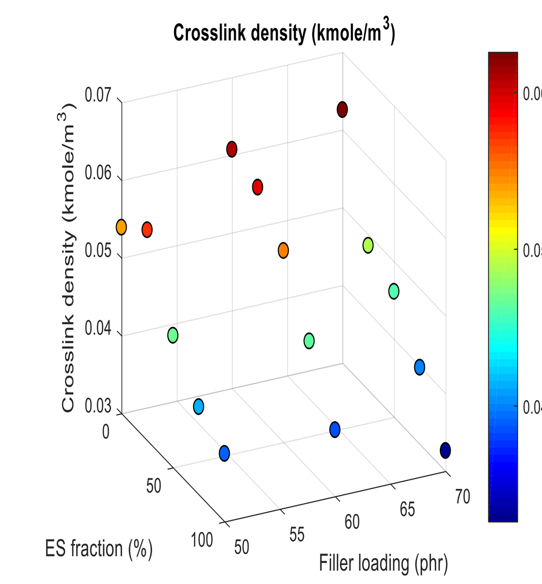


*Fig. 8: Crosslink density of ES/PS filled GNR*

*Table 1: Variables in the statistical model*

| Independent variables/ response variables | Physical meaning (units) |
|---|---|
| $x_1$ | ES fraction (%) |
| $x_2$ | Filler loading (phr) |
| $Y_1$ | Tensile strength (MPa) |
| $Y_2$ | Elongation at break (%) |
| $Y_3$ | M300 (MPa) |
| $Y_4$ | Hardness number |
| a, b and c | constant |

*Table 2: Statistical model for predicting mechanical properties*

| Predicted model | R2 |
|---|---|
| $\frac{x_2}{Y_1} = -0.567 - 0.00311x_1 + 0.06368x_2$ | 0.9677 |
| $\frac{x_2}{Y_2} = -0.023 - 0.00033x_1 + 0.00234x_2$ | 0.9342 |
| $\frac{x_2}{Y_3} = 13.479 + 0.21682x_1$ | 0.9164 |
| $\frac{x_2}{Y_4} = 0.211 + 0.00353x_1 + 0.01036x_2$ | 0.9107 |

- A linear mixed model was developed to predict mechanical properties of ES-PS-GNR composites and, because all $R^2$ were above 0.9 and all parameters were significant, the model accounted for most of the variation (Table 2).

## CONCLUSIONS

ES reinforced GNR significantly more than PS. A small amount of ES improved the PS dispersion and subsequent material properties. However, ES can completely replace PS in GNR and allowed excellent performance of composite materials, combined with a lower cost of manufacture and a lower carbon footprint. If used in tires, the ES composites also have a predicted higher fuel efficiency. These new materials may open new markets for high performance, low cost and sustainable rubber products. Such products may encourage widespread production and processing of guayule in the U.S. Future work will focus on even higher performance applications through ES modification and GNR epoxidation.

## BIBLIOGRAPHY

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2. Barrera, C. S., & Cornish, K. (2016). High performance waste-derived filler/carbon black reinforced guayule natural rubber composites. Industrial Crops and Products, 86, 132–142.

## ACKNOWLEDGEMENTS

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